Emission Control Devices, Fuel Additive, and Fuel Composition Changes

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Emission control devices are installed to meet the exhaust standards of the Clean Air Act for carbon monoxide and hydrocarbons, and it is necessary to know, from a public health point of view, how exhaust emissions may be affected by changes in fuel additives and fuel composition. Since these topics are concerned with developing technologies, the available literature on exhaust emission characteristics and the limited information on health effects, is reviewed.

Introduction

Starting with model year 1975, the method selected to meet exhaust emission standards of the Clean Air Act of 1970 for carbon monoxide and hydrocarbons was the use of the catalytic muffler. With the increasing number of lower compression engines in use and the introduction of the catalytic muffler, sales of the lead fuel additives tetraethyllead and tetramethyllead have been declining since 1970, while the demand for lead-free gasoline, gasoline with different compositions, and fuel additive packages has increased.

Lead exhaust emissions leave deposits on the active metal surfaces of the catalytic muffler that greatly reduce the oxidizing ability or capacity of this emission control device (1, 2). To overcome this problem and greatly reduce lead exhaust emissions without removing lead from gasoline, devices called lead traps were designed and tested (3–5). The device was placed at a position in the exhaust system ahead of the catalytic muffler. Test results (4) showed that the lead trap was capable of removing between 80–90% of lead particulate emissions from exhaust gases for mileage accumulations of up to 100,000 miles. Work to show how the use of the lead trap effects the performance of the catalytic

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muffler in reducing emission rates of cabon monoxide and hydrocarbons is, as yet, incomplete.

It is of public health importance to know how the characteristics of exhaust emissions from motor vehicles will be effected as changes are made in fuel additives and fuel compositions, and as emission control devices are introduced. These topics represent relatively new or developing technologies. The available literature therefore on the identity and characteristics of these exhaust emissions, their environmental transport and transformation, and attendant health effects, is limited. The purposes of this brief survey are to provide a summary of some of the available information on these areas. It is neither an all-inclusive summary nor the final story on these selected topics.

Sulfate Exhaust Emissions from Catalytic Mufflers

The public health impact of the release of sulfate emissions from catalytic mufflers has received considerable attention (6, 7). The increased use of catalytic mufflers on light-duty vehicles resulting in a projected release rate of 0.05 g sulfate/mile was expected to have a considerable health impact on people living near roadways and commuters who suffer from asthma and other acute and chronic respiratory diseases.

One of the first publications reporting on the increase in sulfate emissions from catalytic-equipped

vehicles was that of Campion (8). Since that time, Beltzer et al. (9) and Somers (10) have reported on the measurement of particulate sulfate emission rates for many different makes and models of automobiles equipped with catalytic mufflers.

Cadle et al. (11) have reported the results of the General Motors sulfate dispersion experiment for a fleet of 352 low-mileage 1975 and 1976 catalyst-equipped light-duty vehicles. This was a massive experimental program designed primarily to test the predictive capabilities of the HIWAY Dispersion Model (12) for sulfate exhaust emissions. About 70% of the vehicles were equipped with the pellet-type converters and about 30% were equipped with the monolith-type converters. Of the fleet, 69% were GM vehicles, 17% were Ford Motor Company vehicles, 10% were Chrysler Corporation vehicles, and 4% were American Motors vehicles. The sulfur content of the fuel ranged from 0.028 to 0.032 wt-%. Fuel lead content was between 0.002 and 0.003 g/gal.

The test program was conducted during the month of October 1975 at GM's Milford, Mich. proving ground. The vehicles were driven in packs for 2 hr/day at an average cruise speed of 50 mph to simulate the driving pattern of a four-lane divided highway with a traffic density of 5,460 vehicles/hr. A series of eight 10.5 m sampling towers were situated in the north-south aligned test tract so that one tower was located in the median strip, five were on the east side of the tract, and two were on the west side of the tract. On the west side, the towers were located 2 and 30 m from the edge of the highway, and on the east side of the tract, the towers were located 4, 15, 30, 50, and 100 m from the edge of the highway. A total of 20 flow-through filter samples for sulfate measurement were located on the towers at heights of 0.5, 3.5, and 9.5 m. Average sampling time per sampler was 30 min. Sulfate concentrations were determined by the barium chloranilate method. In addition, measurements of temperature, wind velocities, wind directions, and relative humidity were recorded as a function of height and distance from the highway, for use in calculating stability criteria and dispersion parameters in the HIWAY model. Besides the determination of sulfate concentration by the tower samplers, several vehicles were equipped with syringe samplers to collect in-car sulfate concentrations. For these samplers, the average collection time was 2 hr, the same as the experimental run.

The experimental program was primarily concerned with determining the catalyst sulfate contribution relative to the total measured sulfate concentration. The background levels of sulfate ranged from 0.3 to 19.5 mg/m³. The highest catalyst sulfate level was 15 mg/m³ measured at the 0.5 m height of the median strip tower. On that same day, the background sulfate level was 12.6 mg/m³, the wind was out of the ENE at 0.94 m/sec, the Richardson Number (the ratio of turbulent kinetic energy contributed by buoyant forces to turbulent kinetic energy contributed by shear forces) was 0.338, and the air was stable. The lowest catalyst sulfate level was 3 mg/m³, windspeed was 2.87 m/sec, and the air was unstable. The in-car measurements of catalyst sulfate ranged from 0 to 20 mg/m³, with an average value of 4 mg/m³. In-car levels of catalyst sulfate appeared not to be affected by the vehicle's ventilation system. The average catalyst sulfate level measured at the 0.5 height was 5.2 mg/m³.

The average particle size of catalyst-emitted sulfate was between 0.01 to 0.1 μm. Because of this size range, it was reasoned that emitted particles would disperse as a gas. In studies with sulfur hexafluoride gas (SF_6) a linear correlation between catalyst sulfate concentration and SF_6 concentration was demonstrated for all tower height measurements of these two substances. This correlation made it possible to estimate more accurately the emission rate for sulfate for the fleet since dynamometer tests produced values ranging from 2.6–52 mg/mile. Since catalyst sulfate and SF_6 dispersed in the same manner, the ratio of sulfate emission rate of SF_6 emission rate was constant.

Based on the catalyst sulfate data, contour plots of constant concentration verses vertical and horizontal height were constituted (11). Chock (13) compared these measured values of catalyst sulfate with values determined from the HIWAY model. One of the major assumptions of this model was that the dispersion parameters (δ_y and δ_z) were constant for all stability classes. These assumptions caused the model to overpredict catalyst sulfate concentrations by a large margin at locations far from the test tract. In addition, the model grossly overpredicted catalyst sulfate concentrations for severe meteorological conditions such as low wind speed, extreme stability, and severe temperature inversion. [For more detailed explanation of stability criteria, Richardson Numbers, and atmospheric turbulence, the reader is referred to Lumley and Panofsky (14), Monin and Yoglum (15), Pasquill (16) and Turner (17)]. Empirical relationships to account for variations in the dispersion parameters as a function of stability and distance were suggested by Chock (13) to reduce the gross over-prediction of catalyst sulfate levels at a location far downwind of the source. Petersen (18) in a similar comparative study of the predictive capability of the HIWAY model presented data suggesting that the model predicted sulfate levels within a factor of

two for the immediate vicinity of the highway. The analysis of catalyst sulfate emission data and validations of dispersion models are continuing.

In experiments conducted by EPA and EPA contractors during the GM study, Whitby et al. (19), determined aerosol size distributions for sulfate emissions. Samples were collected on the track with a mobil sample system described in the report. These emissions were characterized by a trimodal-type of distribution: mode 1 was nucleic material, 0.005–0.05 μm; mode 2 was fine material, 0.05–1.0 μm; and mode 3 was coarse material, 1–30 μm. It should be noted that the presence of the majority of material in the fine to very fine particle sizes was unexpected. The release of this fine particulate matter from catalyst equipped vehicles has suggested that more extensive inhalation studies of the health effects of the material are necessary. Tanner and Newman (20) determined that the sulfate emissions were sulfuric acid. It was suggested that this sulfuric acid would react with ambient ammonia to produce $(NH_4)_2SO_4$. These results were preliminary and required additional validation.

The atmospheric transport of particulate sulfur emissions has been studied by Roberts and Friedlander (21) for the Los Angeles Basin. From the transport model used to estimate gas to particle conversion rates for sulfur, it was estimated that the introduction of catalyst-equipped vehicles could add significantly to the particulate sulfur concentrations measured at locations downwind of the release points.

In a study conducted by Exxon Research and Engineering (22), sulfate emission rates for 20 automobiles of various makes and models were determined as a function of accumulated mileage by using the Federal Test Cycle. Average emission rates for the fleet showed a rise from 0.006 g/mile at 0 accumulated miles to 0.021 g/mile at 4000 miles, followed by a decline to 0.006 g/mile at 32,000 miles. The low emission rates at low mileage accumulation were attributed to the sulfate storage phenomena of the muffler, and the decline to lower emission rates at higher mileage accumulation were attributed to the reduction in oxidizing ability of the catalyst. Emission rates for regulated emissions showed CO rates ranged from 4.0 to 5.2 g/mile for 0–32,000 miles; hydrocarbon rates ranged from 0.4 to 0.8 g/mile; and, nitrogen oxides ranged from 1.6 to 1.7 g/mile. The average lead content of the fuel was 0.03 g Pb/gal, and sulfur content had an average value of 300 ppm.

Laresgoiti and Springer (23) have made use of the design equation of plug-flow chemical reactors to explain the conversion of SO_2 produced in the combustion chamber to SO_3 by the catalytic muffler. In this manner, the important design and operating parameters of the system have been identified and placed in a framework which is more susceptible to analysis. From the work of Hammerle and Truex (24) the conversion of SO_2 to SO_3 is a reversible exothermic reaction. Therefore as catalyst temperature rises, conversion of SO_2 to SO_3 decreases. From the analysis of reversible exothermic reactions occurring in plug-flow reactors, Levenspiel (25) has shown that as residence time in the reactor decreases, conversion of reactants to products decreases. Applying these concepts to the catalytic muffler indicates the higher the temperature and the lower the residence time in the reactor, the lower the percent conversion of SO_2 to SO_3. In the EPA studies, which were part of the GM sulfate dispersion experiment (26), for the lower residence times of exhaust emissions in the catalytic muffler associated with an average cruise speed of 50 mph, conversion of fuel sulfur to sulfate was about 12%. The results from the Exxon studies (22) on variation of sulfate emission rate with accumulated mileage, however, would indicate there are other factors involved which affect conversion of SO_2 to SO_3. The use of the plug-flow reactor model, however, does provide a useful beginning.

Lead exhaust emissions can have a severe effect on the oxidizing capacity of the catalytic muffler in reducing emission rates of CO and hydrocarbons. The poisoning effect of the platinum/palladium catalytic surface by the fuel additive package of TEL and the lead scavengers, ethylene dichloride and ethylene dibromide, has been studied by Otto and Montreuill (27). TEL at a concentration of 0.5 g/gal, without scavengers caused the most severe loss of oxidizing ability of the catalytic surface. In this study, oxidizing ability or capacity was related to the amount of Pt/Pd surface area available. For the fuel containing 0.5 g Pb/gal as Motor Mix (both scavengers present) the oxidizing ability of the catalytic muffler after 10,000 accumulated miles, was reduced to about 30% of its original capacity. After 50,000 miles, the oxidizing ability had been reduced to 10% of its original value. These results were compared to unleaded isooctane fuels which did not reduce the oxidizing ability of the active surface at such a rapid rate. In addition, it was shown that the scavenger, ethylene dibromide, caused the most severe but reversible change in oxidizing capacity for CO and hydrocarbon emissions.

Release Rate of Catalyst Components to the Environment

Along with the sulfate emissions, the release of

the components of the catalytic muffler to the environment has been the subject of several experimental studies. The basic components of the muffler are platinum and palladium, about 3 g/muffler, which are applied to an alumnia substrate. The two designs of catalytic mufflers are the monolith and the pelleted reactor.

Brubaker et al. (28) raised the issues of release and fate of platinum in the environment. In the GM study (11), a limited number of determinations of emission rate for platinum were reported. Metal determinations were by atomic absorption and neutron activation. There was no information on chemical form of emitted platinum, and no information on particle size. Taylor and Hanna (29) have reported on the ability of methylcobalamin (MeB-12) to form a moderately stable methylated form of platinum when incubated with micromolar levels of K_2PtCl_6.

Exhaust Emissions from Catalytic Mufflers from the Use of Fuels with Higher Aromatic Content

Gasolines of all grades contain a certain weight percent of aromatic organic chemicals. The chemicals most frequently used are benzene, toluene, and the xylene isomers because they increase the Research Octane Number (RON) and prevent preignition or "knock" of gasoline. The highest percentages of aromatics in unleaded premium fuel are greater than in leaded premium fuels. The major public health concern with the combustion of unleaded fuels containing high weight percents of aromatics is the exhaust emission of particulate matter which has polynuclear aromatic compounds adsorbed to a carbon core (30).

Gross (31) presented data on how exhaust emissions of polynuclear aromatic (PNA) compounds were a function of the engine modification-emission control system, the amount of polynuclear aromatic content of the fuel, and the oil consumption rate. For the 1968 vehicles, the emission control system was an air-injected RAM thermal reactor; the 1970 vehicle control system was a monel + platinum catalytic muffler, Engelhard PTX-5. Emission control systems for 1968 and 1970 model vehicles reduced PNA emissions by 65-85% relative to the uncontrolled vehicle. PNA content in fuel was linearly related to the PNA emission rate. The indicator PNA chosen for identification was benzo[a]pyrene (BaP). High oil consumption caused higher emission rates of polynuclear aromatics.

The major variables affecting BaP emission rate, given by Gross (31) are summarized in Table 1.

Table 1. Variables affecting BaP emission rate

BaP in fuel, ppm	Oil consumption	BaP emission, μg/gal		
		No emission control	1968 engine modification	1970 engine modification
0.01	Normal	130	41	26
0.4-0.5	Normal	290	68	47
3-3.2	Normal	800	200	170
0.4-0.5	High due to valve seal removal	—	—	150
0.4-0.5	High due to oil ring removal	—	7600	—

Previous data from Gross (32) had showed that rate of emission of polynuclear aromatics (PNAs) increased sharply as aromatic content increased from 11% to 46% by weight. Fuel lead and phosphorus content of fuel did not influence emission rates. PNAs tended to accumulate in engine motor oil. The mechanism of PNA emission was similar to emission of lead particulate emission, i.e., a strong function of mode of driving and age of the exhaust system. Other PNAs in exhaust emissions which have carcinogenic potential and have been identified by Grimmer et al. (33) and Boyer and Laitinen (34) are dibenz[a,h]anthracene, chrysene, and benzo[a] + anthracene.

Exhaust Emissions from the Fuel Additive Methylcyclopentadienyl-maganese Tricarbonyl (MMT)

The fuel additive methyl cyclopentadienylmanganese tricarbonyl (MMT) is currently used in the motor mix fuel additive package. It acts as a promoter for TEL and is an antiknock compound in its own right. With the increased demand for unleaded gasoline, the Ethyl Corporation began a major research program to determine the feasibility of the use of MMT in unleaded gasoline. No scavenger compounds would be required, and use concentrations in gasoline would be between 0.0625 to 0.125 g Mn/gal (35–37). At these use levels, the road octane number (RON) of gasoline can be increased by approximately 2.2 units.

Faggon et al. (38) evaluated MMT as an antiknock in unleaded gasoline. Chemically, particulate exhaust emissions from MMT were Mn_3O_4. In extensive dynamometer and road tests, MMT use had no effect on engine performance at the recommended use level of 0.125 g Mn/gal. The use of MMT did not interfere with the oxidizing capacity of the catalytic muffler under realistic operating conditions. In addition, it was demonstrated that

exhaust emissions of benzo[a]pyrene (BaP) were substantially reduced when MMT was added to test fuels. About 0.1% of MMT was emitted to the atmosphere unburned. In prototype lean reactor cars, this level was reduced to 0.01–0.02%. Exhausted MMT was rapidly photolytically decomposed with a half-life less than 2 min. With the use of the Federal Test Cycle, between 20 and 25% of the burned MMT was emitted to the atmosphere and had a mass median equivalent diameter (MMED) between 0.2 and 0.4 μm. With the use of the EPA durability schedule particulate emission rates from gasolines containing 0.125 g Mn/gal averaged 0.097 g/mile.

Ter Haar et al. (39) have studied the photolytic decomposition of MMT in the vapor phase. Major decomposition products were manganese oxides and carbonates. $Mn_2(CO)_{10}$ was not detected. The organic portion of the solid materials appeared to be a complex mixture of acids, esters, and hydrocarbon amorphous polymers resulting from the partial oxidation of the cyclopentadienyl ring, CO insertion reactions, and polymerization of multifunctional compounds. It was estimated that the half life of this reaction was 15 sec.

Using the seven-mode Federal Test Cycle, Ter Haar et al. (39) reported that the average MMED for manganese exhaust emissions from the combustion of fuel containing 0.125 g Mn/gal. were 0.38 μm for cold cycles and 0.30 μm for hot cycles. A comparison with a fuel containing 0.5 g Pb/gal gave an average MMED of exhaust emissions of 0.4 μm for cold cycles and 0.32 μm for hot cycles. It was stated that ⅔ of the exhaust particles from use of the manganese fuel additive were of such a size that they would remain suspended for some time.

There has been considerable concern about the role of airborne manganese in the catalytic oxidation of SO_2 to SO_3. Gerhard and Johnstone (40) found that the photochemical oxidation rate of SO_2 to SO_3 was 0.1–0.2%/hr, the rate being dependent on the relative humidity. Assuming first-order kinetics, this gave a rate constant of about 0.002/hr. McKay (41) studied the atmospheric oxidation of SO_2 in the presence of NH_3. At NH_3 levels of 10 μg/m³, McKay predicted that the conversion of SO_2 to sulfate would be greater than 50%/hr. Again on assuming first-order kinetics, the rate constant was 0.69/hr. Ambient levels of NH_3 have been reported by the PHS (42) are about 20 μg/m³. In simulated atmospheres containing NH_3, SO_2, and manganese particulate emissions, Wright et al. (43) have studied the effect of manganese exhaust emissions on the oxidation of SO_2 in air. It was estimated that if all gasoline contained 0.1 g Mn/gal, this would increase ambient manganese concentrations in

urban air by 0.02 to 0.2 μg/m³. Average yearly ambient concentrations of 0.02–0.05 μg/m³ (44). Wright et al. (43) demonstrated that in their simulated atmosphere in a black bag, manganese concentrations did not have a significant effect on the rate constant for oxidation of SO_2 until levels greater than 20 μg/m³ were reached. Below this concentration, the rate constant was constant at 0.14/hr.

Faggon et al. (38) estimated that the maximum contribution to airborne manganese from use of MMT would be 0.05 mg/m³. A chronic inhalation study with rats and squirrel monkeys at exposure levels of 10, 100, and 1000 mg/m³ for 22 hr/day, 7 days/week, has been reported by Ulrich and Van Petten (45). Thirty rats and eight monkeys were exposed to manganese as Mn_3O_4 with a particle size of 0.2 μm MMED. Rats were sacrificed after 3 and 9 months of exposure, and monkeys were sacrificed after 9 months of exposure. There were no exposure-related changes to the hematopoietic system, CNS, respiratory system, and other tissues examined.

High levels of industrial exposure to MnO_2 particles in air (50,000–60,000 mg/m³) have produced a neurological disorder similar to acute lobar pneumonia (46–56). There is no information on chronic exposure to low levels of manganese oxides both in ambient air and dust and dirt for young children, pregnant women, and segments of the population susceptible to chronic lung diseases.

The parent compound, MMT, has an LD_{50} value of 56 mg/kg by oral administration to mice (57). The TLV (58) for MMT has been given as 0.1 ppm. The geochemistry of manganese, its uptake by plants, and its role as an essential trace element has been reviewed (44).

Alternative Fuels

The use of alternative fuels for gasoline has been suggested and practiced to some extent since the early 1930's. In Europe, particularly, the use of ethanol and methanol blended with gasoline has been a common practice. It has only been recently, however, as a result of uncertain supplies of crude oil that serious consideration has been given to alternative fuel use on a massive scale in the United States.

The NAS (59) has reviewed the status of proposed alternative fuels. The three candidate fuels are liquified natural gas (LNG), hydrogen, and alcohols. Natural gas, composed mainly of methane and propane, is expensive, does not improve drivability, but does offer some advantage over current grades of gasoline in reducing emissions of SO_2 and photoreactive hydrocarbons. Hydrogen offers

many advantages in terms of air pollution reduction since there is no carbon present. Therefore, exhaust emissions of CO and unburned hydrocarbons do not exist. Its high flammability range means that very lean mixtures can be used so that nitrogen oxide emission rates are reduced because of the lower combustion chamber temperatures. Another advantage is the absence of sulfur, thereby eliminating exhaust emissions of SO_2. However, neither the industrial capacity nor the automotive engine-fuel delivery system are available on a large scale.

Alcohols, particularly methanol, alone or blended with gasoline have been used for fuels in spark-ignited engines for some time. Reed and Lerner (60) reviewed the benefits of methanol as a fuel in many applications. As an alternative fuel for gasoline, methanol has a lower heating value and requires the addition of volatile chemicals to aid in starting during cold weather. The main advantage of methanol as a fuel was given by the NAS Report (59) as a reduction of nitrogen oxide emission rates. These lower emission rates were the result of the use of leaner mixtures which produced lower combustion chamber temperatures. This reduction in nitrogen oxide emission rates was supported by the research reports of Adelman, et al. (61), Ebersole and Manning (62), Tillman et al. (63), Most and Longwell (64), and Ingamells and Lindquist (65). However, Bolt (66) and the API (67) contended that the use of alcohols as fuels in automobiles did not appreciably reduce air pollution. This view was supported by Brinkman et al. (68), who demonstrated reductions for CO emissions, but no significant changes in hydrocarbon or nitrogen oxide emission rates for a 10% methanol–90% gasoline blend. In addition, drivability and fuel economy were reduced.

The API (67) report states that use of alcohols results in increased emissions of aldehydes. Aldehydes are very reactive chemicals which can significantly contribute to the atmospheric chemical reactions which convert NO to NO_2 without consuming ozone. This reaction sequence was given by Seinfeld (69) as shown in Eq. (1).
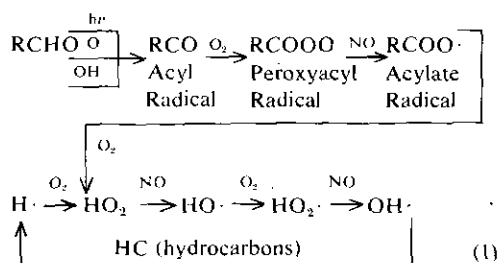
Posner (70) recently reviewed the biohazards of methanol in its proposed new uses. The human biohazards were discussed in eight categories: hazards at young ages; potential interactions; abuse; delayed and irreversible toxicity; dermal and inhalation hazards; toxicity of formaldehyde combustion products; nearly invisible flame; and a larger storage volume required for an equivalent energy return as compared to gasoline. Several suggestions were given to reduce the hazards associated with methanol use, but it was concluded that methanol produced known delayed and irreversible effects and was a difficult chemical to control.

Conclusions

A beginning has been made to review the literature on exhaust emissions from emission control devices, new fuel additives for gasoline, changes in gasoline composition, and completely new fuels. It would be difficult to draw any conclusions on the public health implications of these emissions since these are developing technologies, and, characterization of emissions and toxicology studies are either incomplete or nonexistent. The purposes of this review were to indicate what the most probable and feasible changes would be and to emphasize that they require additional inquiry.

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